PB-216 932

PRESENT STATUS OF CHEMISTRY OF CHLORINE AND AMMONIA-CHLORINE TREATMENT OF WATER

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Cincinnati, Ohio

May 1942

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PB 216 932

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Present Status of Chemistry of Chlorine and Ammonia-Chlorine Treatment of Water

By Assistant Chemist John F. Kachmar

To date the work of the chemical laboratory has been directed toward elucidating the nature of the reaction between chlorine and ammonia, when these two chemicals are present in small quantities in water. This necessitated a bibliographical study of the methods available for the estimation of the various chemical entities involved in the chlorine-ammonia reaction, and also a study of the nature of the chlorine-ammonia reaction itself. Some work on both these aspects is in progress in the laboratory. The bibliographical study is still being continued.

In general, despite much work on the part of a large number of investigators during the last 15 years, the information available on the nature of the chlorine-ammonia reaction is very inadequate and in some ways contradictory. The complexity of the reactions involved and the lack of satisfactory laboratory analytical procedures with which to study the phenomena have retarded rapid progress in understanding the chemical phenomena involved in chloramination. The discovery of the breakpoint phenomena in 1939 stimulated interest in the chlorine-ammonia reaction. However, as pointed out by Calvert(15) further progress in explaining the chlorine-ammonia

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reaction and directing and controlling its efficient use will depend on the development of satisfactory procedures for estimating the chemical entities envolved in the reaction.

A good part of the work done in measuring the bactericidal value of so-called "chloramine" is of limited value because few investigators have been certain of what bactericidal agents were actually present in their water samples. Contradictory results were obtained by different workers, no doubt because they were working with unlike bactericidal agents and under different conditions, but agents which they all termed "chloramine". Bacteriologists will have difficulty in interpreting their results until the chemists make available for them methods for determining just what bactericidal agents are present or formed in water samples dosed with ammonia and chlorine.

The remainder of this report will attempt to summarize the information available on (1) analytical methods and (2) the break-point reaction and to suggest what work need be done at this laboratory.

Analytical Methods

For any adequate study of the chlorine-ammonia reaction and a study of the comparative bactericidal value of chlorine and "chloramine", it would be convenient to be able to determine the following substances in the presence of one another:

1. Free uncombined chlorine (true residual chlorine)
2. Free uncombined ammonia
3. Chlorine combined as chloramines
4. Chlorine combined in other forms (the so-called half-bound chlorine)

5. Nitrogen (ammonia) combined as chloramines

6. Monochloramine, Dichloramine and trichloramine (nitrogen chloride)

7. Other possible chlorine-ammonia reaction products, if present.

1. Methods for Determining True Residual Chlorine

At present two general methods are available for the determination of residual chlorine: (a) colorimetric methods, and (b) the starch-iodide-thiosulfate titration method. The only reagent that has been found satisfactory to date for colorimetric determination of residual chlorine is orthotolidine (O.T.). Tarvin, Todd and Buswell[29] studied a series of 50 organic compounds and found all of them inferior to orthotolidine. Recently Hallinan[7a] has proposed the use of alpha naphthaflavone an absorption indicator, but this has not yet been checked by other investigators. However, the alpha-napthaflavone method merits study because it avoids the interference effects of nitrite, ferric iron and manganous manganese, which effect the O.T. method.

Orthotolidine in its oxidized form can exist either in a yellow form or a blue form depending on the pH of the solution. The yellow form exists at pH values of 2.0 or less and is the common form used in chlorine studies. The blue form exists at a pH of 4.5-5.0 or above and is being used as the basis of automatic control of residual at Montreal[8]. With orthotolidine yellow, there are a number of substances that can give interference effects or false results (NO_2^-, Fe^{+++}, Mn^{++++}). Investigators differ as to the time of contact of reagent and chlorine to obtain the maximum color, the volume, acidity and concentration of the reagent to be used, the concentrations of NO_2^-, Fe^{+++} permissible without obtaining interference. The best evidence

suggests a 10-15 minute contact period in the dark at 20-30° C. with a reagent more acid than that described in Standard Methods[4]. Two ml. of 0.05% orthotolidine in 15% HCl is proposed as against the Theriault[30] recommendation of 1.0 ml. of 0.10% orthotolidine in 10% HCl now described in Standard Methods. However, the low pH in the sample resulting from adding the reagents liberates a portion of the partially bound chlorine and gives results that are not a true measure of the free chlorine in samples containing bound chlorine. It is suggested that a comparative study of the present standard and the proposed more acidic orthotolidine reagent be made, and also that a study of the orthotolidine blue reaction be made, because at the pH at which orthotolidine blue exists (4.5-5.0) NO_2^-, Fe^{+++}, and Mn^{++++} will not interfere (oxidize orthotolidine). It should be understood that a 10-15 min. contact period of reagent and sample will give chloramine chlorine as well as true residual chlorine and possibly some half-bound chlorine. Free chlorine will react with orthotolidine very rapidly, and it would be of interest to know just how rapidly maximum color is developed in samples containing only free chlorine (samples chlorinated to right of break-point). This rapid color development with orthotolidine of samples containing only free chlorine is being used as a test for chlorination beyond the breakpoint[32]. The orthotolidine method has the advantage of being easily adapted to field work.

The starch-iodide-thiosulfate titration method[5] is not adapted to field work; it also requires large samples for analyses and careful technique on the part of the analyst. Different titres will be obtained at different pH values and with differing concentrations of iodide[7]. However, some workers[15,23] prefer it to the orthotolidine method, claiming greater

accuracy; it is accurate at chlorine concentrations greater than 2-3 p.p.m., at which concentrations orthotolidine gives unreliable results without sample dilution. The starch-iodide method has the advantage of being able to indicate whether or not a sample has been chlorinated beyond the breakpoint; to the left of the breakpoint, neutral and acid titrations differ, while to the right of the breakpoint, both titres are alike[15].

In addition to the orthotolidine and starch-iodide methods for chlorine determination the use of p-aminodimethylaniline hydrochloride has been proposed by Kolthoff[33], Alfthan and Jarvis[34] and Haase and Gad[35]. One of the disadvantages in using this reagent is its easy oxidizability which makes the color comparison necessary after a short interval of contact. Byers and Mellon[36] suggest a pH range of 2.6-3.4 for chlorine concentrations up to 0.6 p.p.m. As with the orthotolidine method this low pH will measure not only free chlorine but chloramine and possibly half-bound chlorine. Also Mn^{+++}, and Fe^{+++} will interfere and in the case of the latter element the error is 0.01 p.p.m. chlorine for each 0.1 p.p.m. present according to Byers and Mellon[36].

2. The Estimation of Chloramine-chlorine

Four methods have been proposed for the estimation of chloramine-chlorine. The McNamee test[13], based on measuring the NH_4^+ liberated on acidification of a chloramine solution and calculating back to chloramine chlorine, is not too reliable and requires careful technique (making comparison with standards after one minute color development, when the color is continually changing). The methyl orange[2], methyl red, thymol blue and xylene cyanole[31] decoloration tests depend on the fact that free chlorine

will oxidize very dilute solutions of these indicators, whereas chloramine chlorine cannot. This method is tedious and also requires careful technique. The Griffin[7] test (nitrite test) also depends on the stronger oxidizing power of chlorine, which is able to oxidize nitrite to nitrate whereas chloramine-chlorine cannot. In the test, orthotolidine readings are made on two samples, one untreated and the other treated with nitrite. Hence the test includes all of the weak points of the ortho-tolidine method and requires also a precaution to add only a small excess of nitrite to the sample in order to avoid false ortho-tolidine yellow color formation due to nitrite. The difference in readings of a Nessler tube of sample treated with orthotolidine after 1 min. and 10 min. contact time will also give some measure of the chloramine chlorine. A comparative study of the McNamee, Griffin and time differential ortho-tolidine methods should be made. Some comparative data on the McNamee and time-differential orthotolidine tests has been obtained; the two methods check in about 50% of the samples.

3. The Estimation of Residual Nitrogen

At present there are no dependable methods available for estimating free NH_3 and chlorine NH_3 in chlorinated water samples. Direct Nesslerization of the sample will not necessarily give the free, uncombined NH_3(13). The recovery of total NH_3-N by direct Nesslerization is affected by the magnitude of the chlorine dose.[10] Complete recovery of NH_3-N by direct Nesslerization is obtained only in samples containing chlorine to ammonia in the ratio of less than 2:1[11]. The NH_3-N measured by direct Nesslerization is increased when samples are first dechlorinated with sodium thiosulfate or sodium acid sulfite[15]. The amount of NH_3 obtained by

distillation will be greater than that indicated by direct Nesslerization, but even the amount recovered by distillation will depend on whether or not the sample was previously de-chlorinated prior to distillation. More work along this line is indicated. Wolfe[3] has proposed a method for determining free uncombined ammonia in the presence of chloramines involving the acidification and Nesslerization of two portions of the samples, one having previously been treated with Permutit to absorb the free NH_3. The difference in readings will give the free uncombined NH_3. But this method while simple, has limited value until the significance of Nessler readings on chlorinated samples has been worked out.

The Chlorine-Ammonia Reaction

This is the basic reaction involved in chlor-amination. However, the break-point phenomenon involves in addition the reaction between chlorine and the nitrogen of dead or living organic matter in water. When a sample of water containing NH_3 is chlorinated the residual at first increases with dosages, reaches a maximum, then decreases with further increase in dosage until a minimum or zero residual is obtained and then increases again proportionally with further increase in dosage. This is the break-point phenomenon.

Harvill et al[14] postulate 3 different reactions occurring in the three zones marked I, II, and III. In Zone I the reaction consists of simple chloramination:

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$$

HOCl is formed from Cl_2 + water by the reaction $H_2O + Cl_2 \longrightarrow HOCl + HCl$.

Hence the reaction can be written: $NH_3 + Cl_2 \longrightarrow NH_2Cl + HCl$.

Here both the NH_2Cl and HOCl will give residual chlorine; hence increase of residual with dosage. In Zone II, the chlorine oxidized the chloramine in a dechlorinating action:

$$2NH_2Cl + Cl_2 \longrightarrow N_2 + 4HCl$$

This reaction involves removal of "available" chlorine and hence accounts for decrease of residual chlorine; it also accounts for the decrease in recoverable NH_3-N, because the latter is lost as N_2. When all the free chlorine and NH_2Cl have reacted (at the correct ratio) the water should be free of residual chlorine and recoverable NH_3-N. This has been confirmed by work at this laboratory*. After the break-point, there being no NH_3 available for reaction with Cl_2, the Cl_2 residual should be proportional to further increase in added chlorine.

The ratio of $\frac{Cl_2}{NH_3\text{-}N}$ at the hump is $\frac{71}{14} = 5.07$ (or a ratio of $\frac{Cl_2}{NH_3}$ of $\frac{71}{17} = 4.17$). The ratio of Cl_2 to NH_3 and NH_3-N at the break-point is: (on basis of the reaction)

$$2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl \text{ is}$$

$$\frac{Cl_2}{NH_3\text{-}N} = \frac{213}{28} = 7.6 \qquad \frac{Cl_2}{NH_3} = \frac{213}{34} = 6.28$$

In Zone I up to chlorine-ammonia dose ratio of 4.2:1 it should be possible to recover all NH_3-N unless the dechlorination reaction is occurring to some extent in that zone. The fact that Fresh and Conrad[11] were not able

*Calvert[14a] dissents claiming NH_3 recovery after dechlorination and distillation.

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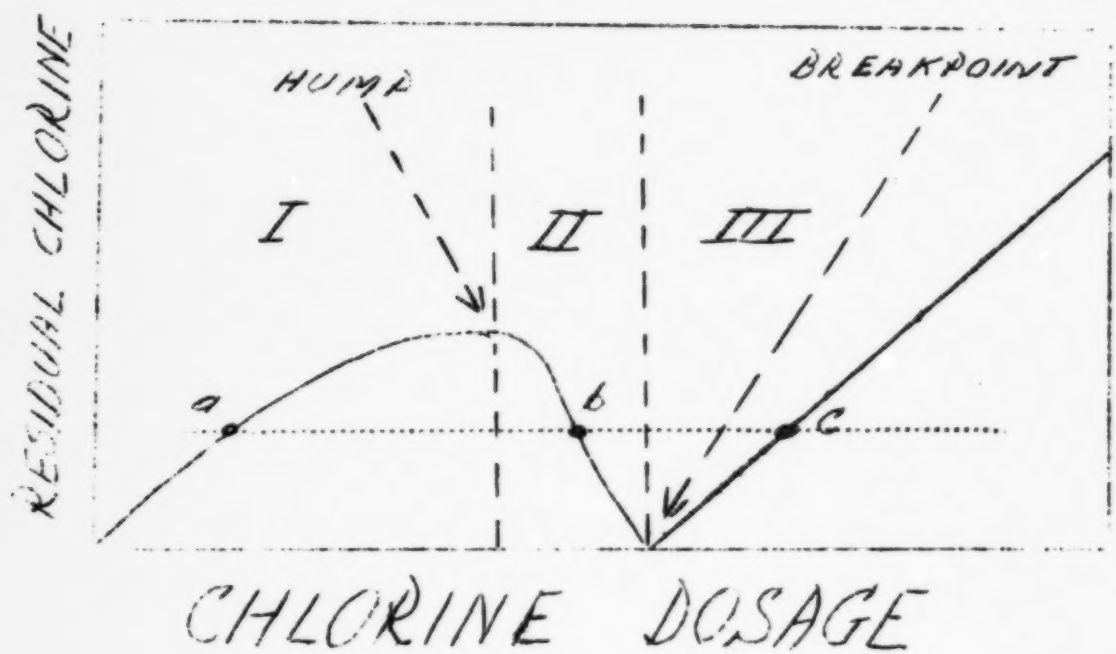
RESIDUAL CHLORINE
HUMP
BREAKPOINT
I
II
III
a
b
c
CHLORINE DOSAGE

to get full recovery of NH_3-N by direct Nesslerization for Cl_2:NH_3 ratios greater than 2:1 indicates that some dechlorination will take place in this zone. This should be verified if possible. In Zone II with excess chlorine no free NH_3 should exist; this also should be verified if possible. Harvill et al actually did obtain break-points at Cl_2: NH_3 ratios of about 6.25 :1. In their experimental work they found no correlation with orthotolidine residual and neutral starch iodide titers for samples belonging to Zone I and II and preferred the neutral starch iodide titers over the orthotolidine determination.

The significant thing is that at points A, B, and C, the sample will have the same residual chlorine value; but at C, all the residual will be present as free chlorine, at B, probably only as NH_2Cl, and at A, probably both NH_2Cl and free chlorine. This also should be verified both chemically and bacteriologically. The bacterial kills are rapid at C but much slower at A and B as shown by Weber et al[17], Mallman et al[23] and others; the chlorine being bound at A and B and all free at C.

Weber, Bendis and Levine[17][18] using ammonia concentrations of 2 and 10 p.p.m. and chlorine dosages 5-40 p.p.m. and 20-200 p.p.m. respectively obtained break-points at $\frac{Cl_2}{NH_3}$ ratios of 7.0-7.9 and 6.8-8.0 respectively. The ratio at the break-point increased with increased amounts of added chlorine. Using a spore-former B.metiens they obtained killing times (minutes required to kill 99% of the organisms) of 83, 88, and 2.7 at points A, B, and C (24.9, 24.2 and 22.5 p.p.m. residual chlorine). Using chloramine ($\frac{Cl_2}{NH_3}$ ratio of 4:1) they found no difference in kill at pH values of 6.7, and

8, but found decreased kill at 5 and 10. The best efficiency lay between pH values of 6-7 for $\frac{Cl_2}{NH_3}$ doses of 4:3.

Griffin and Chamberlin[12] obtained break-point ratios (varying from 10:1 to 9.5:1) of 10:1 $\frac{Cl}{NH_3\text{-}N}$ or $\frac{Cl}{NH_3}$ = 8.25. These values are much higher than those postulated by Harvill et al(7.6 and 6.25 resp.). They found that the removal of NH_2^+ by chlorine depends on pH. This is in direct contradition to the results of Harvill. Griffin found the optimum pH for ammonia removal at 7.0-8.0. They also state that in practice break-point ratios of as high as 15:1 and 25:1 are known. Here we must be careful to distinguish between chlorine required for NH_3 break-point and chlorine required to oxidize other nitrogenous organic materials present in water.[15]

Waters containing nitrogenous materials such as milk wastes, etc., have pronounced break-point curves (with long valleys) whereas a water free of nitrogenous materials will indicate no break-point[12]. Calvert[15] obtained no break-point with egg albumin and gelatin, but obtained degenerate break-point curves with tryptone and peptone (no large initial rise, but a low residual persisting, followed by a slow rise beyond what might be the break-point). With aminoacetic acid (NH_2CH_2COOH) at 15° C. he obtained a rise, followed by a long period of zero residual before the secondary rise began. At 5° C. there was no break-point. NH_3 was liberated from the aminoacetic acid.

Coagulable matter present in water will consume chlorine even beyond the break-point (slow penetration of the material in the floc by the chlorine).

Irwin[21] obtained break-point, ratios (Cl_2:N) of 11:1 and Cl_2:NH_3-N ratios of 5.8:1 at the hump. With nitrite present these increased respectively to 13:1 and 7.5:1. Nitrite is compatible with chlorine in the presence of ammonia to the hump of the curve; beyond this point nitrite is absent. He obtained no break-point and low chlorine absorption with urea and acetamide (0.36 p.p.m.). He claims presence of NCl_3 at the hump of the curve in Zone I, being able to detect it by its odor; this is in contradiction to the supposed non-existence of NCl_3 at pH values above 4.4.

The ability of chlorine to oxidize material in Zone II is used to remove tastes and odors in water supplies, waters chlorinated beyond the break-point, being generally free of all tastes and odors. It has been claimed that chlorine reacts faster with ammonia than with organic matter. Hence the much weaker bacterial killing power of preformed chloramine over freshly formed chloramine, where some free chlorine is available for killing before it reacts with ammonia.

There is evidence that the reaction between Cl_2 and NH_3 takes some time[22] for completion. This needs investigation, and is being studied now in this laboratory. A knowledge of the rate of the Zone I reaction at various pH values should be available.

Chapin[26][27] has shown that with an excess of ammonia present monochloramine alone will exist at a pH of 8.5 or above, a mixture of the di- and mono chloro amines between pH 8.5 and 4.4 (with a 50:50 mixture at 7.0) and only nitrogen trichloride at pH values below 4.4. He also worked out means of separating all three by means of differential extraction with organic solvents. He, however, worked with 1000-2000 p.p.m. chlorine solutions

and with 70,000 p.p.m. ammonia solutions (0.1 M ammonium acetate). The addition of acid to monochloramine will give rise to dichloramine and will free ½ of the bound ammonia.

$$H^+ + 2NH_2Cl \longrightarrow NHCl_2 + NH_4^+$$

Further acidification will form NCl_3 and release additional NH_2^+.

$H^+ + 3NH_2Cl \longrightarrow NCl_3 + 2NH_4^+$ (2/3 of bound ammomia is liberated). Further acidification probably leads to decomposition of the NCl_3.

However, the following reaction has also been postulated to occur by Bodenstein( ).

$3\ NH_2Cl \longrightarrow NH_4Cl + N_2 + 2HCl$ (self decomposition of chloramine, catalyzed by acid and probably by alkali).

Besides N_2 gas also OCl^-, N_2O, NO_2, and NO_3 have been detected as decompostion products. The entire chemistry of the reaction between chlorine and ammonia under various conditions needs review and restudy.

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